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Research on

MBE Growth and Properties of Semiconductor Hetero-Interfaces with Unusual Band Lineups

Final Report

on

ONR Contract N00014-85-K-0669

by

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Abstract

A wide diversity of topics related to various new properties of semiconductor heterostructures were investigated: (a) Staggered-lineup luminescence; (b) Band offsets at lattice-matched (Ga,In)P/GaAs heterojunctions; (c) Optical properties of GaSb/AlSb multi-quantum-well structures; (d) Growth of InAs/GaSb broken-gap heterojunctions; (e) Alternating-beam MBE; (f) Tilted superlattices; (g) Schottky barriers between metals and semiconducting polymers. The determination of the band lineups at the (Ga,In)P/GaAs heterojunction, and the achievement of tilted superlattices by alternating-beam MBE were probably the most significant of these developments. The latter of these two forms the core of research under an ongoing follow-up contract.

1) Research Summary

1.1) General Comments

This two-year contract was a follow-up to the earlier ONR Contract # N00014-77-C-0430, which ran from June 1977 through August 1985, and it was in turn followed up by the new ONR Contract # N00014-87-K-0297, which took effect in September 1987. All three contract had overlapping subject matter, and the present Final Report naturally includes research that was already initiated under the predecessor contract, as well as research that was initiated under the present contract (#0669), but which is still going on.

The research conducted under this contract over a period of two years concerned itself with a wide diversity of topics, all related to various properties of semiconductor heterostructure systems other than the extensively studied (Al,Ga)As system.

1.2) Research Continuing from Predecessor Contract

Staggered-Lineup Luminescence.

One of the successful topics carried out towards the end of the predecessor contract had been the study of below-gap light emission from staggered-lineup heterojunctions (=HJs), specifically p-(Al,In)As/n-InP HJs. This project spilled over into the present contract, with the objective of determining the upper-temperature limit of the phenomenon, and the possibility of achieving (presumably bias-tunable) laser action. The staggered-lineup luminescence was found to decrease rapidly with increasing temperature, and it had disappeared at 125K. Attempts to achieve laser action at liquid-helium temperatures were unsuccessful. The project was therefore not pursued further. As we noted already in the Final Report to 77-C-0430, this topic of below-gap light emission from staggered-lineup heterojunctions has become unusually timely with the discovery that the (Al,Ga)As/GaAs heterosystem is a staggered-lineup system. During the present reporting period this development continued, and we were pleased to see that the staggered-lineup luminescence technique pioneered by us has played a central role in the elucidation of the band lineups in of the (Al,Ga)As/GaAs heterosystem.

We also undertook a search for staggered-lineup luminescence in the GaP/AlP system, which might possibly have a staggered lineup (theoretical predictions are ambiguous for this system). We were not able to observe any evidence for a staggered lineup, but our data do not fully rule out this possibility..

The Lattice-Matched (Ga,In)P/GaAs Heterojunction.

Also still spilling over from the predecessor contract was research on the band lineup in the potentially important lattice-matched (Ga,In)P/GaAs system, which appeared to be an attractive alternative to (Al,Ga)As/GaAs for various kinds of heterojunction devices. Its presumed advantage was that it does not contain aluminum, with its obnoxious affinity for oxygen. On the other hand, being a phosphide rather than an arsenide, it was widely

regarded as a material ill suited for MBE growth. However, we had extensive experience with the MBE growth of GaP (far more than anybody else) and had found GaP a material far easier to grow than its reputation suggested. Hence we felt it essential that the (Ga,In)P/GaAs system be explored. Unfortunately, we found that the ease of growing GaP does not carry over to (Ga,In)P, with its much poorer thermal stability. Although we had great difficulties achieving lattice match, we were in the end able to grow the material. In particular, we were successful in at least one of our main goals: detem ining the band offsets [6], the most important parameters for any use of this heterostructure system, regardless of the technique employed for its growth. This determination had become particularly urgent in the light of the fact that the then-existing theories of the band lineups had all proven unreliable (including our own), and that an experimental value was urgently needed. We found $\Delta E_v = 0.24$ eV and $\Delta E_c = 0.22$ eV, values significantly different than earlier theoretical predictions (0.29 eV and 0.17 eV). Moreover, our values are believed to have an accuracy of better than $\pm$ 0.01 eV!

The technique employed was the C/V profiling technique developed by us under the predecessor contract, and the application of that technique to the (Ga,In)P/GaAs system represents by far the most sophisticated application of the C/V profiling technique, demonstrating beyond a shadow of a doubt its power, and its suitability for a materials system in an early stage of its technological development.

GaSb/AlSb Multi-Quantum-Well Structures.

One of the topics we had studied under the predecessor contract was the growth and properties of GaSb/AlSb multi-quantum well structures. We had turned over some of our samples to the group under Prof. Pilkuhn and Dr. Forchel at Stuttgart University, to perform a variety of optical studies that were beyond our own capabilities. We had originally not intended to continue this work, but as a result of the wealth of new results generated by the Stuttgart group [1]-[5], we relented to Dr. Forchel's pleas for more samples, and prepared another batch. We were rewarded with a torrent of new data [7]-[12]. Of particular significance is the achievement of a great reduction in inter-valence-band absorption and Auger recombination in the multi quantum wells [10], compared to bulk-GaSb. As a result of this cooperation, GaSb/AlSb multi-quantum structures are now almost as well understood as the corresponding arsenide system.

1.3) New Research Topics

InAs/GaSb Broken-Gap Heterojunctions.

One of the main goals at the beginning of this contract had been the study of electron transport *along* the broken-gap p-InAs/n-GaSb hetero-interface. Despite a large effort expended towards this goal, we were not able to achieve it. Although we were able to grow and process the kind of test structures that should have permitted us the determination of transport properties along the interface, we were never able to solve simultaneously the dual contact problem of (a) achieving sufficiently good contact to the electron-hole plasma at the interface, and (b) reduce the leakage between the contacts to the interface plasma and

the other contacts in the structure. All measurements of conductance along the interface were always swamped by leakage currents around that interface, even at cryogenic temperatures. Towards the end of the contract we had to conclude that our goal was probably unachievable with existing technology, and we gave up.

Despite this very disappointing outcome, the project had significant beneficial fallout that made it far from a total loss: (a) It greatly increased our understanding of the MBE growth of both InAs and GaSb, especially the temperature conditions of such growths. (b) As a result of the need to dope GaSb n-type, we developed the doping technique using a PbTe 'captive' source into a fairly reliable routine technique [14], which has since then proven to be unexpectedly effective for AlSb as well. Both of these developments have proven very fruitful in our InAs/AlSb quantum well work that was at the time sponsored by the Semiconductor Research Corporation, and which has since then become an important and successful project under the successor contract to the present one.

Alternating-Beam MBE.

At the 1986 MBE Symposium in York, England, Briones et al.[1] reported on RHEED oscillations during MBE growth with a periodic interruption of the As flux with a period roughly equal to the monolayer growth period. His data suggested to us that the Ga atoms have a very high surface diffusivity while the As beam was turned off, and that it might in this way be possible to lower the growth temperature of GaAs and AlAs or to improve the crystal quality at a given growth temperature. We set out to study this possibility, going almost immediately beyond Briones, by interrupting the Ga (and Al) beam as well, in such a way that there was only one beam on at any instant of time. We were in this way able to reduce the growth temperature for GaAs to about 200°C and that for AlAs to about 300°C.

Tilted Superlattices.

Early in 1987, progress with the alternating-beam MBE scheme described above suggested the use of this scheme to realize an old 1984 proposal by Petroff et.al.[2] , for the growth of "vertical superlattices." The idea requires (a) a perfectly periodically stepped starting surface, and (b) an epitaxial growth mode that proceeds purely by the addition of atoms to step edges, with no nucleation on the step surfaces away from the edges. Stepped surfaces are easily obtained by cutting the substrates with a deliberate misorientation from the [100] direction toward one of the [011] directions. (A 2° misorientation gives step widths of 80Å on a GaAs surface if all steps are exactly one monolayer high). In the postulated growth mode, a fractional monolayer of one material (e.g. GaAs) is deposited on the surface, then

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[1] F. Briones, D. Golmayo, L. Gonzáles, and A. Ruiz, "Phase-Locked RHEED Oscillations during MBE Growth of GaAs and $Al_xGa_{1-x}As$," J. Cryst. Growth, 81, 19-25 (1986). — [Proc. 4th Int. Conf. on Molecular Beam Epitaxy, York, UK, Sept. 1986]

[2] P. M. Petroff, A. C. Gossard, and W. Wiegmann, "Structure of AlAs-GaAs interfaces grown on (100) vicinal surfaces by molecular beam epitaxy," Appl. Phys. Lett.45, (#6), 620-622 (Sept. 1984)

diffuses to the step edges, and finally bonds to the substrate, resulting in a fractional stripe-like coverage at each step. Then, a fractional monolayer of a second material (e.g. AlAs) is deposited in the same manner. If the monolayer fractions of GaAs and AlAs add up to exactly one complete monolayer, then continued growth in this manner will produce a vertical superlattice as shown in Fig. 1.

A combination of conventionally grown horizontal layers and vertical superlattices would allow two-dimensional control of crystal composition. For instance, quantum wires could be produced by placing a short section of vertical superlattice between two conventional barrier layers.

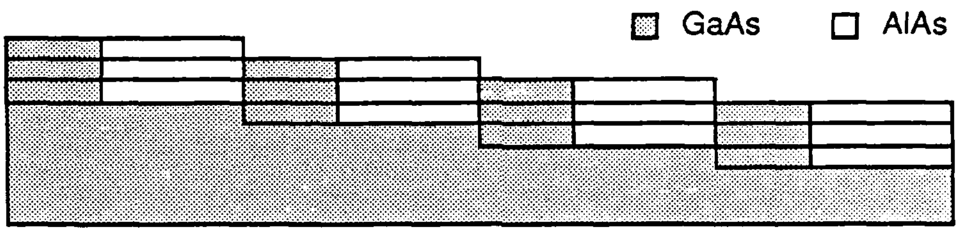

Fig. 1. Ideal growth of $(GaAs)_{0.4}(AlAs)_{0.6}$ vertical superlattice after deposition of 3 monolayers.

Petroff et al. had been unsuccessful in their attempts to grow the vertical superlattice, indicating that the simple growth procedure described above was not operating. By the time the present contract had expired, we had not yet succeeded in achieving the desired structure, but we had a breakthrough shortly thereafter, under the follow-up contract [15]. Details will be reported in the reports to that contract.

Organic/Inorganic Heterojunctions.

Professor Alan Heeger in the Physics Department at UCSB is one of the world's leading experts in conducting organic polymers. He and the P.I. were approached by a student wishing to study the electronic events at interfaces between conducting organic polymers and conventional semiconductors like GaAs. It was an irresistible opportunity, and we decided to take on the student for a joint project of this kind, with Prof. Heeger providing 2/3 of the support, and this ONR contract the remaining 1/3. Initial work was on polythiophene, on its characterization, and on initial measurements of the I-V and C-V characteristics of aluminum Schottky barriers to this material. Doped with ClO_4 ions, the material is a good p-type conductor, exhibiting good rectification characteristics to Al, but not to Au or Pt.

However, various properties of polythiophene made it an unsatisfactory material to work with. We subsequently made a very fortuitous switch in the model polymer with which to conduct our research on organic/inorganic heterojunctions, to poly-3-hexylthiophene (P3HT), a recently discovered *soluble* semiconducting polymer, the contact properties of which have not been previously studied. Films of P3HT can be cast from solution, which

makes it possible to deposit films onto insulating substrates, a necessity for many applications and even for many measurements. After working out the casting conditions, excellent In/P3HT Schottky diode I - V characteristics were obtained, as good as the best previous In/P3MT diodes, as well as good straight-line $1/C^2$ - vs -V plots [13]. **Table 1** shows device parameters extracted from the capacitance data.

TABLE 1: *Junction parameters extracted from capacitance-voltage data.*

	In/P3HT	In/P3MT
N_a (cm^{-3})	$3x10^{16}$	$7x10^{16}$
V_{bi} (V)	0.61	0.76

Superconductor/Semiconductor Heterostructures.

With the discovery of the new high-T_c superconductors, our attention was naturally drawn to these materials. The new high-T_c superconductors are more reminiscent of heavily doped semiconductors than of ordinary metals. This similarity suggests that it might be a useful heuristic principle actually to view these superconductors *as if* they were fairly conventional semiconductors, for the purpose of discovering some of the electronic device potential of these materials. Ultimately, this analogy will of course break down, but it appears a promising point of departure, and even the inevitable ultimate breakdown of the analogy is likely to reveal much about these materials. More specifically, we were intrigued by the idea of superconductor/semiconductor "heterojunction" interfaces, with an emphasis on the study of *interactions* between the electrons in the two different kinds of materials, of the kind that might lead to new kinds of phenomena of potential interest for future electronic devices.

However, during 1987, before any substantial amount of work had been started under this contract, we were able to secure separate DARPA/ONR funding for this superconductor/-semiconductor work, and no further work was undertaken under the present contract.

2) Publications

The following published papers, listed in chronological order by publication date, describe work that was supported at least partially under this contract, except that the first four papers in the list describe work that was supported under the predecessor contract, but which had not appeared yet at the time of the Final Report to that contract, and had not been included in that Final Report.

[1] "Optical Gain in GaSb/AlSb Multi Quantum Well Heterostructures" (by B. Maile, E. Zielinski, H. Schweizer, G. Griffiths, K. Mohammed, S. Subbanna, H. Kroemer, and J. L. Merz), MRS - Europe 1985, pp. 41-46.

[2] "Indirect and Direct Gap Recombination in GaSb/AlSb Multi Quantum Well Structures," (by U. Cebulla, A. Forchel, G. Tränkle, H. Kroemer, G. Griffiths, S. Subbanna, and J. Wagner), MRS - Europe 1985, pp. 161-166.

[3] "Recombination effects and laser properties of GaSb/AlSb multiple quantum well structures," (by E. Zielinski, H. Schweizer, B. Maile, M. H. Pilkuhn, G. Griffiths, S. Subbanna, and H. Kroemer), Proc. 1985 Int. Symp. GaAs and Related Compounds, Karuizawa, Japan; Inst. Phys. Conf. Ser., Vol.**79**, pp. 749-750, 1986.

[4] "Size-Induced Direct-to-Indirect Gap Transition in GaSb/AlSb Multiple Quantum Well Structures," (by A. Forchel, U. Cebulla, G. Tränkle, H. Kroemer, S. Subbanna, and G. Griffiths), Surf. Sci., Vol. **174**, pp. 143-147 (1986). [Proc. 2nd Int. Conf. (Yamada Conference) on Modulated Semiconductor Structures (MSS-II), Kyoto, Japan, Sept. 1985].

[5] "$2E_g$ - Transitions in GaSb/AlSb Quantum Well Structures," (by A. Forchel, U. Cebulla, G. Tränkle, E. Lach, T. L. Reinecke, H. Kroemer, S. Subbanna, and G. Griffiths), Phys. Rev. Lett. **57** (#25), pp. 3217-3220, Dec.1986.

[6] "Determination of valence and conduction band discontinuities at the (Ga,In)P/GaAs heterojunction by C-V profiling," (by M. A. Rao, E. J. Caine, H. Kroemer, S. I. Long, and D. I. Babic), J. Appl. Phys., Vol. **61** (#2), pp. 643-649, Jan. 1987.

[7] "$E_0 + \Delta_0$ transitions in GaSb/AlSb quantum wells," (by A. Forchel, U. Cebulla, G. Tränkle, U. Ziem, H. Kroemer, S. Subbanna, and G. Griffiths), Appl. Phys. Lett., Vol. **50** (#5), pp. 182-184, Jan. 1987.

[8] "Verification of Direct-Indirect Cross-Over in GaSb-Al-Sb MQW's by Time Resolved Spectroscopy," (by U. Cebulla, A. Forchel, G. Tränkle, S. Subbanna, G. Griffiths, and H. Kroemer), Physica Scripta, Vol. **35**, pp. 517-519, 1987. [Europ. Phys. Soc. Meeting, Stockholm, March 1986]

[9] "Optical Spectroscopy on $E_0 + \Delta_0$ Transition in GaSb/AlSb Quantum Wells," (by U. Cebulla, U. Ziem, G. Tränkle, A. Forchel, G. Griffiths, S. Subbanna, and H. Kroemer), Superlattices and Microstructures, Vol. **3** (#1), pp. 1-4, 1987. [Proc. 2nd Int. Conf. Superlattices, Microstructures, and Microdevices, Gotenborg, Sweden, 1986]

[10] "Enhanced T_0 - Values in GaSb/AlSb - Multi Quantum Well Heterostructures," (by H. Schweizer, E. Zielinski, S. Hausser, R. Stuber, M. H. Pilkuhn, G. Griffiths, H. Kroemer, and S. Subbanna), IEEE J. Quant. Elect., Vol. **QE-23**, pp. 977 - 982, June 1987. [Proc. 10th IEEE Semicond. Laser Conf., Kanazawa, Japan, 1986].

[11] "Spectroscopic Investigation of the Properties of III-V Quantum Well Structures at High Densities," (by G. Tränkle, A. Forchel, E. Lach, H.Leier, M. H. Pilkuhn, G. Weimann, H. Kroemer, and M. Razeghi), Proc.1986 Int. Symp. GaAs and Related Compounds, Las Vegas, Nevada, USA, Inst. Phys. Conf. Ser., Vol **83**, pp. 221-226, 1987.

[12] "Optical Spectroscopy of $2E_g$ - Transitions in GaSb/AlSb Quantum Wells," (by A. Forchel, U. Cebulla, G. Tränkle, T. L. Reinecke, H. Kroemer, S. Subbanna, and G. Griffiths), Proc. 18th Int. Conf. Phys. Semicond. 1986, Stockholm, pp. 573-576; World Scientific Publishing Co. Singapore, 1987.

[13] "Metal-Polymer Schottky Barriers on Cast Films of Soluble Poly (3—alkylthiophenes)," (by H. Tomazawa, D. Braun, S. Phillips, A. J. Heeger, and H. Kroemer), Synthetic Metals, Vol. **22**, pp. 63-69, 1987.

The following paper, submitted and published after the expiration of this contract, describes work performed and essentially completed under this contract.

[14] "N-Type Doping of Gallium Antimonide and Aluminum Antimonide Grown by Molecular Beam Epitaxy using Lead Telluride as a Tellurium Dopant Source," (by S. Subbanna, G. Tuttle, and H. Kroemer), J. Electron. Matls., Vol. **17** (#4), pp. 297-303, 1988.

The following paper, which has not yet appeared in print, describes work the early parts of which were supported by the this contract.

[15] "MBE Growth of Tilted GaAs/(Al,Ga)As Superlattices by Deposition of Fractional Monolayers on Vicinal (001) Substrates," (by J. M. Gaines, P. M. Petroff, H. Kroemer, R. J. Simes, R. S. Geels, and J. H. English), J. Vac. Sci. Technol.

3) Scientific Personnel Supported under this Contract, And Degrees Earned

3.1) Principal Investigator

Professor Herbert Kroemer: Throughout entire contract period.

3.2) Post-Doctoral Research Associates

Dr. Ernie J. Caine: From beginning of contract until April 30, 1986.
Dr. James Gaines: From Oct. 15, 1986 until end of contract; continuing under follow–up ONR contract.

3.3) Research Assistants working towards a Ph.D. Degree

Mr. Seshadri Subbanna: Throughout entire contract period; continuing towards Ph.D. under follow-up ONR contract.
Mr. David Braun: Since Sept. 1986; continuing towards Ph.D. under follow-up ONR contract. (supervised jointly with Prof. Heeger)
Mr Muralidhar Rao: Since May 1987; continuing towards Ph.D. under follow-up ONR contract. (supervised jointly with Profs. Hu and Long)

3.4) Research Assistants working towards an MS Degree

Mr. Bryan Jasper (Summer 1986)

3.5) Individuals Contributing to this Research without Financial Support

Professor James L. Merz, advisor and contributor to photoluminescence work.